



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

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For: SEPARATOR FOR LITHIUM ION SECONDARY BATTERY AND LITHIUM ION SECONDARY BATTERY PROVIDED THEREWITH

DECLARATION UNDER 37 CFR §1.132

COMMISSIONER FOR PATENTS

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U.S.A

Sir:

I, Masahide SUGIYAMA, hereby declare and state that:

1. I am a citizen of Japan, 3-1, Mochimunetomoe-cho, Shizuoka-shi, Shizuoka-ken, Japan
2. I am one of the inventors of the subject application, and I am fully familiar with the subject matter thereof as well as the references relied upon by the Examiner in the prosecution of this application.
3. I obtained a Master's degree in science and engineering from Ibaraki University in March 1996.
4. I am currently employed by Tomoegawa Paper Co., Ltd., and began working

for Tomoegawa Paper Co., Ltd., on April 1, 1996, in development research at Shizuoka establishment.

5. I conducted the following experiments.

### **I. Object**

With regard to the references (Pekala et al. U.S.Pub. 2002/0142214 and Oka et al. U.S. Patent 5,830,603) which were cited in the Advisory Action (dated January 5, 2006) issued on the present application (U.S. Patent Application, No.10/659,358), tests were conducted to provide supplemental data showing that significant effect of the present invention can be obtained when the separator for the lithium ion secondary battery has the external surface of an average pore size of 0.1 to 5  $\mu\text{m}$  and the interior of an average pore size of 0.5 to 10  $\mu\text{m}$  in the porous layer, and the average pore size of the external surface is less than that of the interior, and that such an effect cannot be obtained by the separator disclosed in the references. It was shown that an effect equal to that of the present invention cannot be obtained when the separator disclosed in the references is used.

### **II. Example**

Examples 7, 8 and 11 which are cited below are described in the present specification.

#### **[Example 10-1]**

In the same manner as in Example 8, except 12 parts by weight of PFVd having a weight-average molecular weight of about 300,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

#### **[Example 10-2]**

In the same manner as in Example 8, except 8 parts by weight of PFVd having

a weight-average molecular weight of about 300,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

[Comparative Example 6-1]

In the same manner as in Example 8, except 10 parts by weight of PFVd having a weight-average molecular weight of about 150,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

[Comparative Example 6-2]

In the same manner as in Example 8, except 2 parts by weight of PFVd having a weight-average molecular weight of about 300,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

[Comparative Example 6-3]

In the same manner as in Example 8, except 10 parts by weight of PFVd having a weight-average molecular weight of about 300,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

[Comparative Example 6-4]

In the same manner as in Example 8, except 8 parts by weight of PFVd having

a weight-average molecular weight of about 1,000,000 were used as PFVd constituting the porous layer, and a separator with the porous layer formed on both surfaces was obtained. The resulting various physical properties of the separator were measured and evaluated in the same manner as in Example 7. The results are shown in Table 4-1.

Table 4-1

	Thickness of porous layer <sup>1)</sup>	Average pore size of interior	Average pore size of external surface	Air permeability sec/100 ml	Weight of porous layer	Impregnation ratio of electrolytic solution <sup>2)</sup>	Retention properties of electrolytic solution <sup>3)</sup>	Ionic conductivity (25°C)
	μm	μm	μm		G/m <sup>2</sup>	% by weight	% by weight	S/cm
Example 10-1	1.5/1.5	9.3	4.6	120	1.3	65	61	$5.1 \times 10^{-3}$
Example 10-2	1.5/1.5	0.7	0.2	180	1.5	58	75	$2.8 \times 10^{-3}$
Comparative Example 6-1	1.5/1.5	11.1	4.6	110	1.2	70	45	$3.8 \times 10^{-3}$
Comparative Example 6-2	1.5/1.5	9.5	5.4	120	1.2	52	22	$6.5 \times 10^{-3}$
Comparative Example 6-3	1.5/1.5	0.4	0.2	460	2.1	41	68	$7.1 \times 10^{-4}$
Comparative Example 6-4	1.5/1.5	0.7	0.09	1450	2.4	27	73	$2.1 \times 10^{-4}$

<sup>1)</sup> thickness of one surface/thickness of another surface

<sup>2)</sup> (weight of separator after impregnation - weight of separator before impregnation)/weight of separator after impregnation × 100 (%)

<sup>3)</sup> (weight of separator before standing - weight of separator after standing)/weight of separator before standing × 100(%)

In the same manner as Example 11, simple test cells of Examples 15 to 16 and Comparative Examples 11 to 14 were produced by using the separators obtained in Examples 10-1 to 10-2 and Comparative Examples 6-1 to 6-4.

(Evaluation of test cell)

With respect to the test cell thus obtained, charge and discharge cycles were repeated 50 times. After comparing an initial discharge capacity with a discharge capacity after 50 cycles, a capacity retention ratio was calculated. After 50 charge and discharge cycles, the test cell was disassembled and adhesion between the separator and electrodes was visually observed. The results are shown in Table 5-1.

Table 5-1

	Kind of separator used	Volume retention ratio <sup>1)</sup> (%)	Adhesion <sup>2)</sup>
Example 15	Example 10-1	> 95	A
Example 16	Example 10-2	> 95	A
Comparative Example 11	Comparative Example 6-1	68	B
Comparative Example 12	Comparative Example 6-2	58	B
Comparative Example 13	Comparative Example 6-3	65	B
Comparative Example 14	Comparative Example 6-4	40	B

1) discharge capacity after 50 cycles/initial discharge capacity × 100 (%)

2) A (excellent): firmly adhered

B (ordinary): partial peeling or space observed

C (poor): total peeling or space observed

### III. Result

As shown in Table 4-1, Examples 10-1 to 10-2 provided a significant effect of both impregnation ratio of electrolytic solution and retention properties of electrolytic solution to obtain excellent ionic conductivity of  $10^{-3}$  or more.

In contrast, Comparative Example 6-2 to 6-4 do not achieve a good effect of either impregnation ratio of electrolytic solution or retention properties of electrolytic solution, and thus ionic conductivity was reduced so as not to be obtain ionic

conductivity of  $10^{-3}$  or more. Comparative Example 6-1 could obtain ionic conductivity of  $10^{-3}$  or more, but there was problem in view of evaluation of test cell as described below because the average pore size of interior is large.

As shown in Table 5-1, the simple test cells using the separators produced in Examples 15 and 16 maintained high capacity retention ratios even after 50 cycles, while the simple test cells using the separators produced in Comparative Examples 11 to 14 showed drastic reduction in capacity.

With respect to adhesion between electrodes and the separator after 50 cycles, in the test cells of Examples 15 and 16, electrodes firmly adhere to the surface of the separators of Example 10-1 to 10-2 provided with a porous layer containing a vinylidene fluoride resin as a main component and it was difficult to easily peel the electrodes. In the test cells of Comparative Examples 11 to 14, partial peeling was observed and the electrolytic solution oozed out at the portion.

As is apparent from these results, retention properties of the electrolytic solution deteriorate and the electrolytic solution oozes out from the interior of the separator to cause peeling, even if the separators have a layer containing a vinylidene fluoride resin as a main component and this layer is contacted with electrodes, unless it is controlled such that the external surface of the layer has an average pore size of 0.1 to 5  $\mu\text{m}$ , the interior of the layer has an average pore size of 0.5 to 10  $\mu\text{m}$ , and the average pore size of the external surface is less than that of the interior.

#### **IV. Conclusion**

As shown in the above results, the present invention provides a significant effect by the external surface having an average pore size of 0.1 to 5  $\mu\text{m}$  in the porous layer, the interior having an average pore size of 0.5 to 10  $\mu\text{m}$  in the porous layer, and the average pore size of the external surface being less than that of the interior.

Therefore, the significant effect of the present invention is not anticipated by the references in which the above specific ranges of the average pore size of the external surface and the interior are not disclosed.

Accordingly, if the references are combined, the separator disclosed in the references is not within the scope of claim 1 of the present application.

6. I understand fully the content of this declaration.
7. The undersigned declares further that all statements made herein of his own

knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of this application or any patent issuing thereon.

8. Further declarant saith not.

  
Masahide SUGIYAMA

April 5, 2006

Date